



Integral waterproof concrete: A comprehensive review

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ABSTRACT

The ingress of water and aggressive substances is the primary reason for the chemical and physical degradation of concrete infrastructure, leading to a reduction in durability and a shortening of life span. In practice, different integral waterproofing admixtures and surface coatings have been widely used to prevent or mitigate this problem. Compared with surface protection, the incorporation of integral waterproofing admixtures (such as densifiers, water repellents, and crystalline admixtures) in concrete has several benefits, such as ease of application, elimination of regular maintenance, and little or no deterioration over time. So far, there is no comprehensive review on integral waterproofing admixtures and their effects on various properties of concrete. This review examines existing literature on integral waterproof concrete containing various commercial and laboratory-made waterproofing admixtures. This comprehensive review highlights that the use of integral waterproofing admixtures has the potential to increase the service life and improve the durability of concrete structures and infrastructure. However, the admixtures may have a negative impact on some concrete properties, such as workability and strength. Whilst many hydrophobic and crystalline admixtures can reduce the water absorption rate of concrete by up to 80%, they often have a negative impact on the concrete compressive strength, causing a strength reduction of about 10% or more. Their influence on some durability properties (e.g., reinforcement corrosion, microbial-induced concrete corrosion) is inconclusive, indicating the need for further research. There is also a need to develop proper guidelines to determine the efficacy of integral waterproofing admixtures. More research is also required to assess the long-term performance of integral waterproof concrete and its benefits based on life cycle assessment.

1. Introduction

Concrete is inherently porous and has numerous microcracks in the matrix, making it vulnerable to the ingress of water and other aggressive fluids. A reduced life span over time is expected for concrete infrastructure exposed to an aggressive environment because of physical and chemical degradation [1]. Likewise, concrete infrastructure located near the groundwater table or in a highly humid environment is also susceptible to deterioration due to the ingress of water [2]. Without intervention, significant maintenance for critical infrastructure is required with high associated repair costs. To reduce/eliminate the need for maintenance, suitable measures can be adopted to significantly reduce the water absorption rate of concrete [3–5].

Currently, there is no universally accepted definition for waterproof concrete (also known as water-resistant and watertight

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concrete). The German Committee on Reinforced Concrete [6] defines waterproof concrete as that with a water absorption rate reduced by more than 50% in comparison to untreated reference concrete. According to the National Corporation of Highway Research Program in the USA [7], the water absorption rate of waterproof concrete should be less than 2.5%. In the British Standard [8], it is stated that waterproof concrete should have the ability to prevent moisture movement from one place to another. Despite the different definitions, it is clear that waterproof concrete should have a relatively low water absorption rate.

Various measures have been adopted to reduce the water absorption of concrete. Traditional methods include adding supplementary cementitious materials (SCMs) to the concrete mixture, reducing the water-to-cement (w/c) ratio, and using additional reinforcement to control concrete cracking. More recently, researchers proposed a few other methods for developing waterproof concrete, such as the use of external membranes, surface coatings, or integral waterproofing [1,9]. In particular, the use of integral waterproofing admixtures has been considered a viable alternative to the other commonly used waterproofing methods [1]. In this regard, many different integral waterproofing admixtures have been tried, and the findings show that their effectiveness in reducing water absorption varies significantly [10].

The use of integral waterproofing admixtures aims to turn the concrete itself into a water barrier. In contrast, external membranes or surface coatings only form a barrier on the top or bottom surface of the concrete. Therefore, integral waterproof concrete does not require regular maintenance and can be used in structures, such as deep foundations and tunnelling works, where it is challenging to apply a layer of protection [11]. Furthermore, the effectiveness of coatings and waterproof membranes is susceptible to surface damage or concrete cracking during the service life [1]. Once damaged, the water absorption rate and permeability of the concrete increase dramatically [12,13]. However, the permeability of integral waterproof concrete will not be affected by any surface worn out. Thus, integral waterproof concrete could potentially have improved durability performance than concrete with a surface protection layer [1]. But additional measures should be adopted to prevent water ingress at concrete joints or locations with the potential to develop large cracks.

Integral waterproofing admixtures in liquid or powder form can be incorporated into concrete in batching plants. Such admixtures can be classified into three categories: densifiers, water repellents (also known as hydrophobers), and crystalline admixtures. Densifiers refine the pore size distribution of concrete and densify the cement matrix, whereas water repellent admixtures change the surface tension within cracks and pores to raise the liquid contact angle, thereby resisting absorption [14,15]. In contrast, crystalline admixtures are reported to increase concrete resistance against water penetration under pressure by pore blocking arising from solids deposition through chemical reactions [16]. The most widely used densifiers are various SCMs, such as silica fume, fly ash, and slag. The efficacy of these densifiers in decreasing concrete water absorption has been well established, but they can seldom reduce water absorption by over 30%. Thus, the developed concrete by only adding SCMs cannot be recognised as waterproof concrete [17]. Therefore, this review will mainly focus on concrete with hydrophobic and crystalline admixtures. Typical hydrophobic admixtures include silicone-based compounds, fatty acids, calcium stearate, and fats and oils. Recently, crystalline chemicals (e.g. sodium acetate) have also been used in concrete due to their capability to enhance the concrete's self-sealing properties [16].

Table 1 summarises recent review articles [3,4,18–21] published on waterproof concrete to demonstrate the need for the present review paper. As can be seen in this table, most of the previous review articles are focused on surface coating technology and its effects on the mechanical properties and long-term durability of concrete. There is no comprehensive review on the effects of various integral waterproofing admixtures on concrete behaviour. Accordingly, the objectives of this paper are threefold. First, the mechanisms and limitations of various integral waterproofing admixtures will be reviewed based on the current state of knowledge of the interaction between the integral waterproofing admixtures and concrete. Second, the effects of integral waterproofing admixtures on the concrete's fresh, mechanical and durability properties will be critically analysed. Finally, crucial insights and recommendations for further

Table 1
Recent review articles on waterproof concrete.

Published year/applied method	Discussed topics	Reference
2017/Surface coating, impregnation, pore blocking surface treatment and multifunctional surface treatment	<ul style="list-style-type: none"> • Influence of several hydrophobic mechanisms on concrete surface protection, such as air permeability, bonding strength and cracking resistance 	[18]
2018/Nano-engineered surface coating	<ul style="list-style-type: none"> • Effect of surface microstructure on hydrophobic performance • Long-term performance of nanoscale hydrophobic surface coating 	[19]
2018/Hydrophobic admixture	<ul style="list-style-type: none"> • Influence of hydrophobic admixture in reducing the water absorption of concrete • Mechanism of hydrophobic process 	[20]
2021/Surface coating	<ul style="list-style-type: none"> • Relationship between hydrophobic agent quality and concrete substrate properties • Effect of hydrophobic agent and w/c ratio on the carbonation resistance of concrete substrate • Influence of hydrophobic agent and w/c ratio on chloride resistance of concrete substrate 	[21]
2022/Surface coating and internal treatment	<ul style="list-style-type: none"> • Fabrication of superhydrophobic concrete: surface and bulk modification • Durability of superhydrophobic concrete such as water impermeability, corrosion resistance, anti-icing ability and freeze-thaw resistance, UV resistance 	[3]
2022/Surface coating and internal treatment	<ul style="list-style-type: none"> • Hydrophobic modification based on templating, coating, and internal methods • Stability of hydrophobic coating on the surface of cement-based materials • Influence of hydrophobic modification on cement hydration, strength, waterproofing, chloride ion penetration, freeze-thaw, and carbonation of cement-based materials • Application of hydrophobic modification of cement-based materials 	[4]

research will be made.

The review conducted in this study utilised a combined approach of systematic and scoping review methods to map and critically analyse recent studies. The initial stage of the review involved creating research questions and then identifying relevant keywords. The research questions were: ‘What are the waterproofing mechanisms of different integral waterproofing admixtures’, and ‘what are the effects of integral waterproofing admixtures on the concrete properties’. The research questions’ relevant keywords were then identified, and the scientific databases were searched using the following keywords: Waterproof concrete; Hydrophobic concrete; Watertight concrete; Water-resistant concrete; Water-repellent concrete; Hydrophobic admixtures; Waterproofing admixtures; Damp proofing admixtures; Waterproofing additives; Mechanical properties of waterproof/hydrophobic/water repellent concrete; Durability of waterproof/hydrophobic/water repellent concrete; Fresh properties of waterproof/hydrophobic/water repellent concrete; etc. To gather relevant publications, scientific databases such as Scopus, Web of Science, ScienceDirect, and Google Scholar were searched. The search identified approximately 2350 research articles, and a review was conducted on 130 selected articles that were closely related to the research questions. The article selection was based on specific selection criteria by excluding articles that were not published in English and removing duplicate articles. Finally, the full texts were evaluated to select the most relevant papers. This method is similar to that used in many other recent scientific reviews. Fig. 1 illustrates the outline of this study and the main aspects that have been reviewed.

2. Research significance

Substantial research has been conducted over the past decades on the development and application of different waterproofing admixtures and surface coatings/membranes for concrete protection. There are a few existing review articles in this area that summarise the research outcomes of surface coatings/membranes. However, to the best of the authors’ knowledge, there is no review paper on integral concrete waterproofing admixtures and their effects on various properties of concrete. It is necessary to review various waterproofing admixtures and chemicals based on the mechanisms of developing water resistance. The present study addresses this gap. Accordingly, the waterproofing admixtures are categorised based on their waterproofing mechanisms, and the influence of these admixtures on the fresh, mechanical, and durability properties of different types of concrete is discussed. Requirements for future research as well as the challenges and limitations of using waterproofing admixtures in concrete are also presented. This review will expand the prospects of researchers and engineers who are closely associated with the concrete waterproofing industry. Comprehensive data were used to assess the impact of various types of integral waterproofing admixtures on the concrete properties.

3. Integral waterproofing admixtures

This section will briefly review different types of integral concrete waterproofing admixtures and the associated limitations. The mechanisms of different admixtures to achieve waterproofing have been studied thoroughly in Refs. [14,15,22–33] and are summarised in Table 2. Fig. 2 summarises the advantages and disadvantages of integral waterproof concrete against concrete protected by other waterproofing methods.

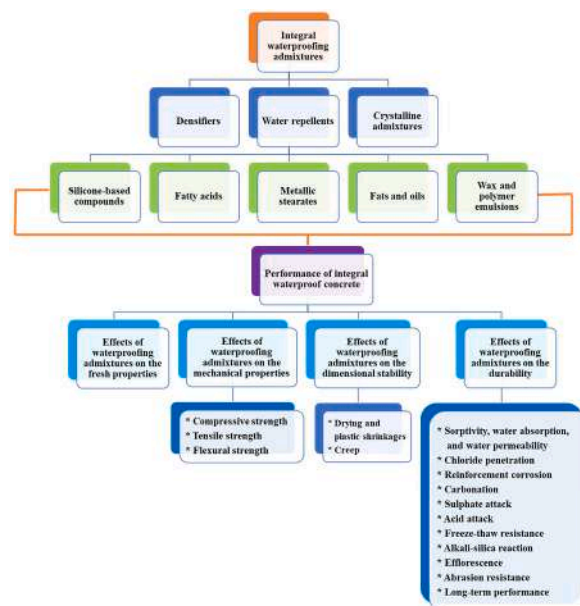


Fig. 1. An overview of this study.

Table 2
Mechanisms and features of different types of integral waterproofing admixtures.

Type	Mechanisms		Features	Typical admixtures
Densifiers	React with the calcium hydroxide produced in hydration and create by-product materials, slowing water migration and increasing concrete density		<ul style="list-style-type: none"> • Not characterised as waterproofing or hydrophobic materials since they cannot seal joints and cracks. • Under hydrostatic pressure, it requires additional waterproofing treatment to preserve concrete from degradation and damage. • Concrete overall cost can be reduced by using appropriate proportions in the mix design. • Can be used as a partial replacement of Portland cement. 	Slag, fly ash, metakaolin, rice husk ash, silica fume, nano-SiO ₂ , nano-Al ₂ O ₃ , nano-Fe ₂ O ₃ , and fluorosilicate-based admixtures [14,15,22]
Water-repellents	Silicone-based compounds	Waterproofing admixtures develop polymer barriers inside pores during the hydration process. These admixtures typically exist in liquid form and include long-chain fatty acids (LCFA) derivatives, stearates, oils, and hydrocarbons. Performance of these compounds is highly reliant on the concrete itself.	<ul style="list-style-type: none"> • Usually used in massive concrete structures, including bridges, marine applications and airports. • Can be found in the form of liquid emulsions or as powder additives [23]. • Prevent concrete from breathing due to the alkoxy group that forms its molecular structure [24]. • These products have a detrimental impact on the environment and natural resources as their main component is made from organic materials [25]. • Expensive and poor wear resistance [26,27]. 	Everdure Caltite, Conqor B52, and Hycrete are some of the commercially available water-repellent admixtures.
	Fatty acids	Neutralised fatty acid salts are used as hydrophobic admixtures.	<ul style="list-style-type: none"> • Sometimes these types of admixtures produce a wax-like compound that coats the capillaries surface during the evaporation process, which results in hydrophobic behaviour. • A contact angle of 180° has been achieved with this method [28]. 	Solid fatty acid, especially stearic acid, is extensively utilised as a hydrophobic admixture. Liquid fatty acids, including caprylic, oleic, and capric acids, can also be used as hydrophobic admixtures.
	Metallic stearates	One of the basic properties of metallic stearates is water repellency.	<ul style="list-style-type: none"> • Reduced permeability and bulk and capillary water absorption have been reported for concrete incorporated metallic stearate under non-hydrostatic conditions [29]. 	Calcium stearate, aluminium stearate, and zinc stearate
	Fats and oils	Vegetable oils can be applied as a hydrophobic admixture for concrete and mortar if an appropriate distribution is obtained by dispersing the oil in water before blending.	<ul style="list-style-type: none"> • A relatively small quantity (0.5-1.5% of cement weight) is needed. • Oils with a high amount of monounsaturated fatty acids appear to be the most influential. • Rapeseeds oil seems to be the most attractive option from a concrete technology perspective, mainly as it can be produced in cold climates [30]. 	Rapeseed, peanut, silicone and olive oils.
Crystalline admixtures	Wax and polymer emulsions	Finely divided wax emulsions are influential hydrophobic admixtures. Emulsions break down after contact with alkaline water in concrete pores and form a hydrophobic layer.	<ul style="list-style-type: none"> • A reduction in compressive strength of 4% could be observed when added at the proportion of 3% to the binder (cement) [31]. 	Waxes with a melting point range of 57-60 °C are used with an emulsifying agent based on ethoxylated sorbitan monostearate or sorbitan monostearate.
		Unlike hydrophobic counterparts, crystalline admixtures use available water to grow crystals inside the concrete – efficiently sealing off the moisture pathways.	<ul style="list-style-type: none"> • These admixtures are hydrophilic in nature and exist in a dry, powdered form. • Crystalline technologies have self-sealing ability. • Crystals within the concrete are invulnerable to physical deterioration and damage; there is no danger of tears, punctures, or seam leaks. 	Sodium acetate [32,33].

3.1. Densifiers

Most densifiers can react with calcium hydroxide $[\text{Ca}(\text{OH})_2]$ generated in cement hydration, creating another product that increases concrete density and slows water migration. Since densifiers are less effective than water repellents and crystalline admixtures in reducing water absorption, some researchers do not consider densifiers as waterproofing admixtures [10,15]. Nonetheless, densifiers can still slow water migration in concrete matrix and are often used in combination with water repellents or crystalline admixtures to develop waterproof concrete.

The most widely used densifiers in concrete are SCMs and some nanomaterials (e.g., nano- SiO_2 , nano- Al_2O_3 , and nano- Fe_2O_3). The effects of these materials on the fresh, mechanical and durability properties of concrete have been well studied [14,34]. It is generally believed that pozzolanic reactions of SCMs change the microstructure of concrete and the chemistry of the hydration products by consuming the released calcium hydroxide and producing additional calcium silicate hydrates (C-S-H). This leads to increased strength and reduced porosity and therefore improved durability [35]. It has been reported that a more uniform and compacted microstructure was created after incorporating nano- SiO_2 in normal concrete (see Fig. 3) [36]. As nano- SiO_2 has very high activity due to its galactic specific surface area, it can react with $\text{Ca}(\text{OH})_2$ crystal quickly to produce C-S-H gel, which fills the voids to enhance the density of the interfacial transition zone (ITZ) and the binding paste matrix. As can be seen in Fig. 3b, a large amount of C-S-H gel has been formed in concrete containing nano- SiO_2 , which cannot be seen in the reference paste without nano- SiO_2 . Therefore, the stability and integration of the hydration product structure are enhanced, leading to improved durability and long-term mechanical properties of concrete. Other types of nano particles, such as Fe_2O_3 and Al_2O_3 , also have similar filler effects and/or pozzolanic activity on the

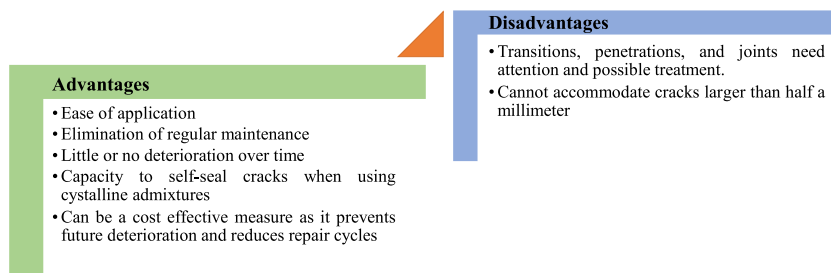


Fig. 2. Advantages and disadvantages of integral waterproofing admixtures.

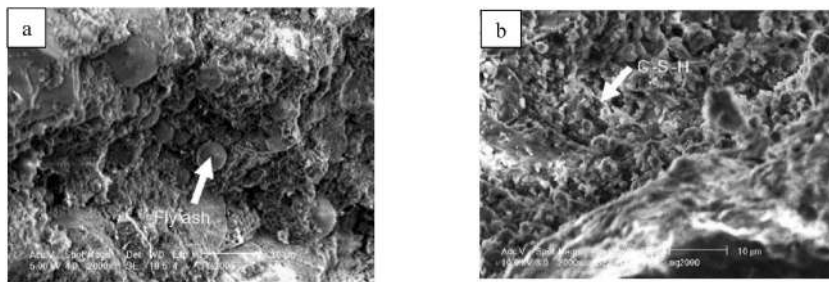


Fig. 3. Microstructure of normal concrete incorporating fly ash: (a) without nano- SiO_2 ; and b) with nano- SiO_2 [36].



Fig. 4. Water-repellent impregnated natural zeolite [38].

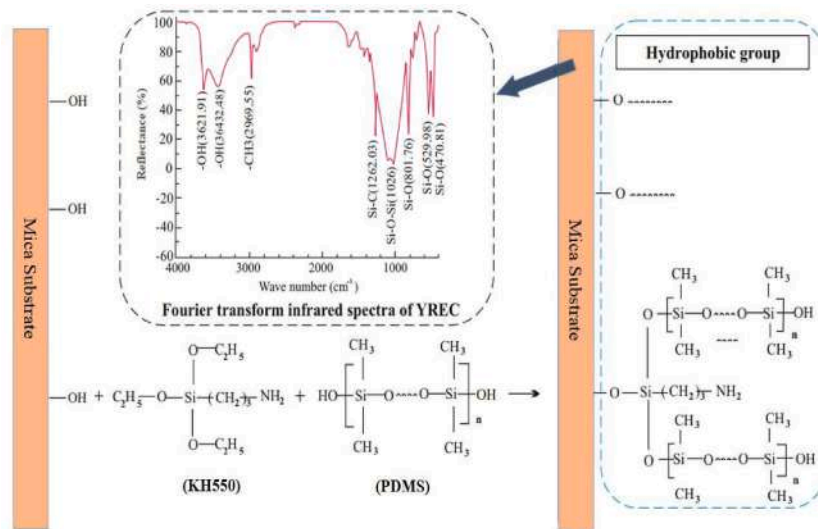


Fig. 5. Coupling mechanism of mica and PDMS using a silane coupling agent [39].

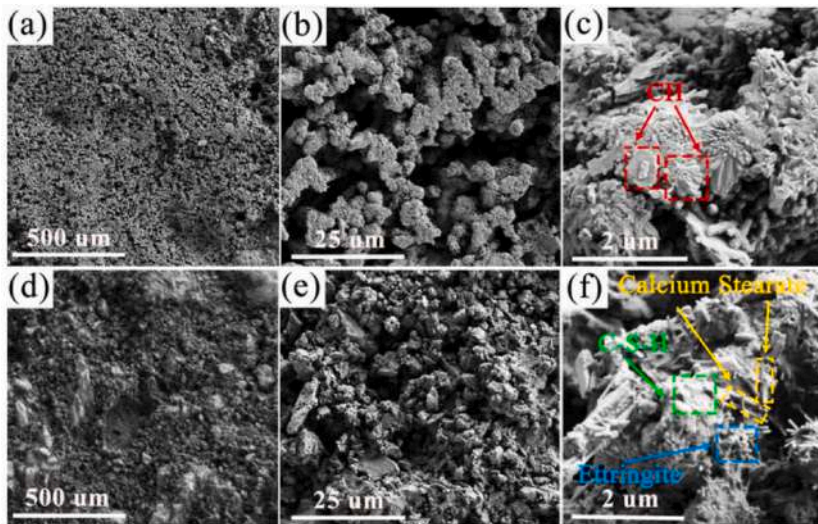


Fig. 6. Surface morphology: (a-c) untreated concrete; and (d-f) treated concrete [43].



Fig. 7. Concept of turning waste newspaper into an admixture for producing hydrophobic concrete [9].

cementitious matrix [34]. It should be noted that concrete with densifiers normally has limited self-healing capacity. Thus, such concrete may not be suitable for sealing joints or cracks.

3.2. Water repellents

Water repellents, also known as hydrophobic admixtures, alter concrete's surface tension, making it inherently non-absorptive and water-repellent. Therefore, the contact angle for pore walls can be increased to 90° or above, preventing water penetration into the pores. According to the ACI report [37], hydrophobic admixtures may not resist water penetration under hydrostatic pressure if not

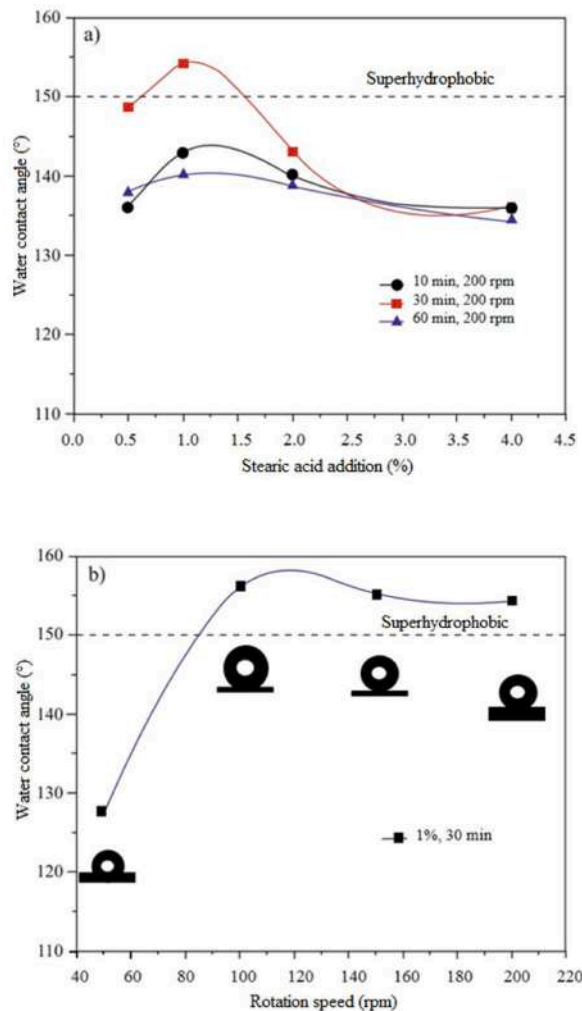


Fig. 8. Hydrophobic GGBS powders: (a) effects of stearic acid content and milling time; and (b) effect of milling speed [26].

used in combination with other admixtures. Therefore, these admixtures are most suitable for non-critical areas with low water tables or above-ground applications. Different types of water repellents are summarised in Table 2 and reviewed as follows.

3.2.1. Silicone-based compounds

In the last 20 years, silane and oligomeric siloxane started to be used as integral water-repellent agents. They can be formulated as liquid emulsions to be used in mortar and concrete or as powder additives to be directly added to dry mixes [23]. The silane serves to wholly block the pores, preventing concrete from breathing due to the alkoxy group that forms its molecular structure. Some recent research has examined the impact of silane/siloxane-based products on the environment, highlighting their detrimental impact on the environment as their main component is made from organic materials [25]. Furthermore, silanes are expensive [26] and can lead to poor wear resistance of the produced concrete [27]. Another problem related to silane/siloxane-based products is the possible material separation and heterogeneity when they are incorporated directly into concrete. The material separation is caused by the difference in specific gravity between the concrete and the water repellent. Thus, it is challenging to uniformly disperse the hydrophobic component in concrete. To address this issue, Yoon and Lee [38] prepared cement mortars by mixing 1%, 3%, and 5% ZWR (Zeolite + silane-siloxane-based impregnation) in cement powder. The produced ZWR demonstrated excellent hydrophobicity, as shown in Fig. 4. The ZWR-treated concrete samples also exhibited superior durability properties, such as water penetration, carbonation, and chloride resistance, compared to the untreated concrete.

More recently, Zhu et al. [39] developed a water-repellent agent (YREC) to improve the crack resistance of concrete in dry curing conditions. The water-repellent agent was developed by mixing 1% waterproofing polydimethylsiloxane (PDMS) with 1% KH550 silane coupling agent and 98% mica with a lamellar structure. Fig. 5 displays the mechanism of KH550 in coupling PDMS to the mica powder. It was suggested that a surface treatment at 150 °C for 15 min would be beneficial for achieving a robust water-repellent effect. Another silicone-based material is silicone resin that works by coating the inner walls of concrete pores with a film to repel water [40]. When incorporated into concrete, a silicate gel forms and coats the capillary pores of concrete [41,42].

3.2.2. Fatty acids

Diluted or undiluted liquid fatty acids, including caprylic, oleic, and capric acids, can be used as hydrophobic admixtures in a concrete mix. In particular, solid fatty acid, i.e., stearic acid, has been extensively utilised as a hydrophobic admixture and can be added directly to concrete in powder form [43]. Fig. 6 shows the scanning electron microscopy (SEM) images of concrete treated with and without stearic acid. As can be seen, the pore size of the untreated concrete is larger than that of the treated concrete. The treated concrete had a rough and convex structure, as shown in Fig. 6d and (e). The rough structure consisted of acicular ettringite and fine calcium stearate, as can be observed in Fig. 6f. Under the influence of stearic acid, the hydrated product is superimposed with a needle-like structure that can make the concrete rough to create the Cassie-Baxter state, which is essential for the concrete to maintain superhydrophobicity [43]. Stearic acid can also be premixed with inert fillers, like silica or talc or an emulsion in water to help dispersion throughout the mix [31]. Furthermore, it can also be used as a modifying agent to produce hydrophobic waste-based sand to substitute natural sand in mortar or concrete [44,45]. Song et al. [44] recently used 7% stearic acid as a modifying agent to prepare superhydrophobic oyster shell powder. Mortar with 30% replacement of the superhydrophobic oyster shell powder showed a water contact angle of 95.2° . In another study [45], 1.5% stearic acid was reported to be the optimum amount to modify iron ore tailings, and 30% hydrophobic iron ore tailings powder was added to mortar to achieve the hydrophobic state. However, although such water repellent agents are considered economical, they often have a negative impact on the mechanical properties of concrete, limiting their wide application in practice.

Pre-treated hydrophobic admixtures can also be made with fatty acids and used to improve the water repellent property of concrete. Hydrophobic paper sludge ash (PSA) and ground granulated blast furnace slag (GGBS) powders have been converted into hydrophobic powders by milling with stearic acid to functionalise the powders [9,26]. The concept of turning waste newspaper into a hydrophobic admixture and then developing hydrophobic concrete is indicated in Fig. 7. It was reported that the dry ball milling speed and time had substantial impacts on the hydrophobic performance of such hydrophobic powders, as shown in Fig. 8. Therefore, optimisation is required to find out the optimal milling speed and time and the type and ratio of raw ingredients. Thus, the quality control of the hydrophobic admixtures in mass production could be challenging. In recent research conducted by the authors [10], different hydrophobic powders (e.g., GGBS, fly ash, and glass) treated with 2% stearic acid were prepared and used to develop hydrophobic concrete. Although the water absorption rate of the treated concrete could be reduced by up to 30%, it was still too high to meet the water absorption limits specified for waterproof concrete in Refs. [6,7]. Shi et al. [46] also developed a hydrophobically modified steel slag using stearic acid via chemical treatment, and the slag with 1% stearic acid improved the water contact angle of the treated mortar up to 91.5° .

3.2.3. Metallic stearates

Stearates, such as calcium stearate, aluminium stearate, and zinc stearate, are derived from fatty acids and are readily available for use in concrete. They can provide a hydrophobic coating to capillary pores and consequently restrict water transfer in concrete under non-hydrostatic conditions [47]. According to the authors' recent research [10], calcium stearate might be a promising material for developing integral waterproof concrete. It reacts with water and cement to produce a hydrophobic wax-like product, which coats the surfaces of capillaries after water evaporation. Besides, calcium stearate often has a particle size ranging from nanometres to a few microns, which can also seal micropores in concrete [47]. Most stearates, such as calcium stearates, have a negative impact on the workability and mechanical properties of concrete. Nonetheless, these negative effects could be mitigated by adding other admixtures, such as superplasticisers and SCMs.

3.2.4. Fats and oils

Fats and oils can also be used as hydrophobic admixtures in concrete. Natural fats and vegetable oils consist primarily of glycerides (i.e., esters of glycerol and fatty acids) along with minor amounts of other lipids [48]. Glyceride (like other esters) is chemically unstable in the highly alkaline environment of concrete/mortar. It hydrolyses into glycerol and fatty acid anions by consuming three hydroxyl ions in the process. The carboxyl group -COO^- of the fatty acid anion coordinates firmly with calcium. Thus, the fatty acid anion is kept inside the concrete/mortar, and water repellency is formed due to the hydrophobic portion of the molecule. Nevertheless, fats and oils have detrimental effects on the mechanical properties of concrete, limiting their wide application in practice [30,49].

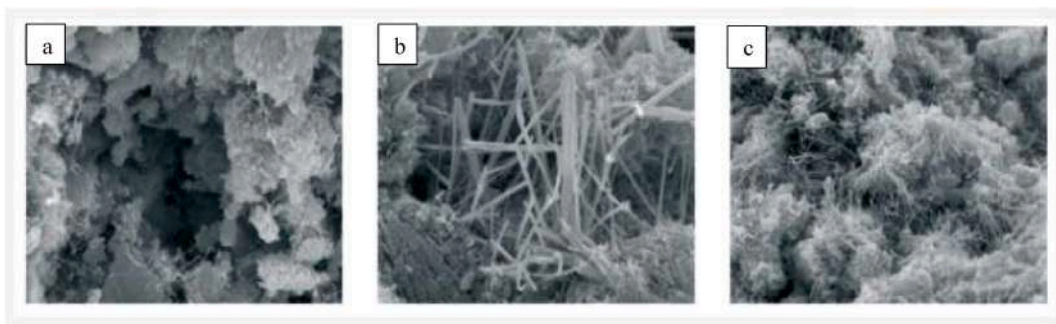


Fig. 9. Crystalline waterproofing admixture in concrete: (a) voids; (b) crystal growth in voids; and (c) sealed voids [50].

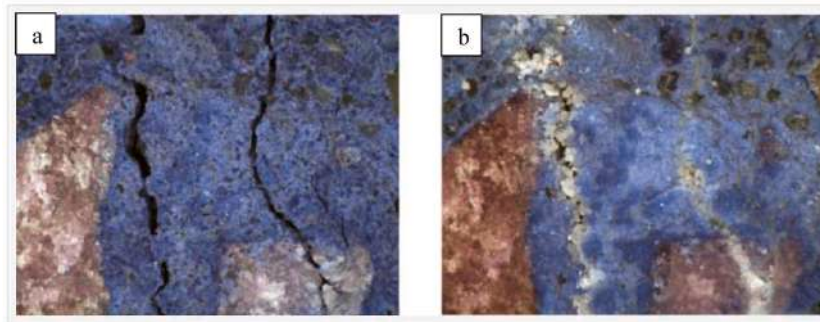


Fig. 10. Self-healing of shrinkage cracks: (a) formation of shrinkage cracks; and (b) cracks healed by nanocrystals [51].

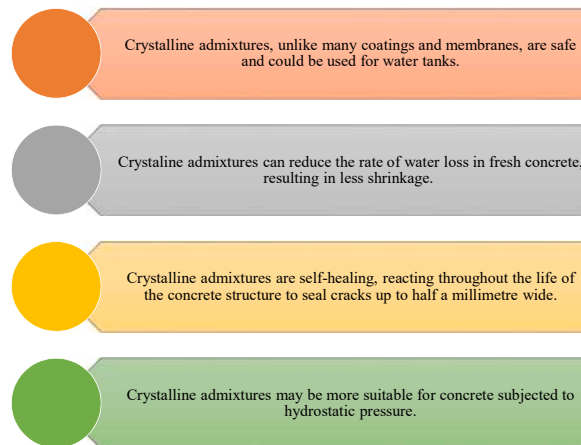


Fig. 11. Advantages of crystalline admixtures against other waterproofing admixtures.

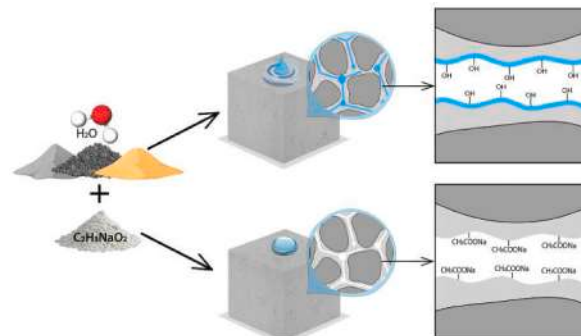


Fig. 12. Bonding and interaction between concrete and sodium acetate [52].

3.2.5. Wax and polymer emulsions

Very finely divided wax emulsions are potential water repellents for concrete. The emulsion breaks down after contact with the alkaline pore water in concrete and forms a hydrophobic layer after coalescence. Waxes with melting points in the range of 57–60 °C have been employed with an emulsifying agent based on ethoxylated sorbitan monostearate or sorbitan monostearate [31]. The emulsifying agents could be categorised as esters, and they will hydrolyse in an analogue manner to butyl stearate. Furthermore, latex as an emulsion of synthetic polymers can also be used as a water repellent. The latex can coalesce into a continuous film, forming a stronger network than waxes. However, it should be noted that latices are relatively expensive, and a dosage of up to 5% is needed to have noticeable benefits [31].

3.3. Crystalline admixtures

Many commercial waterproofing products are based on crystalline admixtures. The crystalline chemicals used in these products are kept confidential by all producers. In academic studies, sodium acetate is commonly used as a crystalline admixture. The crystalline-

based systems typically exist in a dry powdered form and are hydrophilic in nature, which means they absorb water. Unlike their hydrophobic counterparts, crystalline systems use available water to grow crystals inside the concrete, closing off pathways for moisture to seep into the concrete. In contrast to water repellents, crystalline technologies are reported to enable self-sealing after a crack is generated, as penetrated water can trigger new crystal growth to seal the crack [33]. Therefore, the concrete with self-sealing ability becomes a water barrier again, as shown in Fig. 9 [50]. When the moisture content in concrete is low, voids can be clearly seen in the concrete (Fig. 9a). After absorbing water, crystals start to grow in the voids, as can be seen in Fig. 9b. After a certain period, the voids are mostly sealed by formed crystals, as shown in Fig. 9c. It has been reported that crystalline formulas can seal hairline cracks with a width up to 0.51 mm [51], which can be seen in Fig. 10. Fig. 11 summarised the potential benefits of crystalline admixtures over other waterproofing admixtures. However, a few researchers have reported that some commercial crystalline admixtures reduced the mechanical strength of concrete, which will be further discussed in Section 4.

As a typical crystalline admixture, sodium acetate has been recommended to extend the service life of concrete and improve its durability without affecting its strength [32,52]. Fig. 12 shows the interaction between concrete and sodium acetate to form waterproof concrete. However, according to the authors' research [10] and results reported by others [42,53], the water absorption rate of concrete with sodium acetate is greatly affected by its w/c ratio. Hence, to develop waterproof concrete in practice by using sodium acetate, trial tests should be conducted to choose a suitable amount of sodium acetate for concrete with a specific w/c ratio. Otherwise, sodium acetate may even negatively increase the water absorption of concrete if the amount of sodium acetate is not optimal. Besides, sodium acetate takes time to form crystals. Therefore, it may not be effective for early-age concrete. Moreover, according to unpublished research conducted by the authors, sodium acetate is more effective in reducing the water absorption rate of concrete when it is dissolved in the mixing water than used in powder form to mix with other solid ingredients. Dissolving in water might improve the dispersion of sodium acetate in the concrete mixture.

Based on the above discussion, the following points can be drawn:

- Densifiers should be used in simple structures as they cannot seal joints and cracks. These admixtures can be used as a partial replacement for Portland cement.
- Water-repellent admixtures can effectively increase the water contact angle, but they often decrease the mechanical strength of concrete.
- Using crystalline chemicals, such as sodium acetate, might be an effective method of improving concrete's waterproofing properties to some extent if properly used. They are reported to heal new concrete cracks in the service stage as well.
- Several studies suggested the use of hybrid admixtures, such as the combination of water-repellent and crystallising admixtures. However, extensive studies should be conducted to evaluate the financial and technical feasibility.

Among different waterproofing admixtures, silane/siloxane-based products, stearates, and crystalline admixtures are getting popular among concrete practitioners. Nonetheless, the selection of a waterproofing admixture should consider the service conditions and required performance of the structure. Meanwhile, the influence of the waterproofing admixture on the fresh, mechanical and durability properties of the concrete should also be considered. For example, when a structure is exposed to a small or no hydrostatic pressure, densifiers and/or water repellents are often sufficient to reduce water penetration. However, hydrophilic crystalline chemicals such as sodium acetate might be more suitable for structures under hydrostatic conditions if properly used [24].

4. Performance of integral waterproof concrete

Although the main purpose of adding waterproofing admixtures in concrete is to reduce its water absorption rate, these admixtures may also affect various fresh, mechanical, and durability properties of concrete.

4.1. Effects of waterproofing admixtures on the fresh properties

Workability is one of the most frequently studied fresh properties of integral waterproof concrete, which is important for the proper placement and consolidation of fresh concrete. It has been reported that the addition of silane-based water repellents [54] and black olive oil [55] could increase the workability of concrete. A study conducted by Leong [56] revealed that adding calcium stearate into lightweight foamed concrete did not affect the workability of fresh concrete with an optimum w/c ratio of 0.60. However, a recent study by the authors [10] revealed that calcium stearate reduced the slump by up to 20% for normal concrete with a w/c ratio of 0.53.

Several researchers reported increased workability after adding more than 2% crystalline admixture in concrete without observing thermal cracking or segregation [52]. Similar results were also reported by Al-Kheetan et al. [57] for normal concrete with the inclusion of 2% or 4% sodium acetate despite the relatively high w/c ratios (i.e. 0.46 and 0.53). Furthermore, the workability of fresh concrete was reported to increase by nearly 33% when a multi-crystallisation enhancer (MCE) was applied to ready-mix concrete [58]. This is attributable to the MCE's ability to disperse the cement particles. The inclusion of a pre-treated hydrophobic admixture might increase or decrease the workability of concrete, depending on the type and dose of the admixture. For example, concrete workability increased with increasing hydrophobic GGBS [26]. However, this was not true for concrete with hydrophobic paper sludge ash (PSA), where the workability of concrete decreased with an increasing amount of hydrophobic PSA due to the porous nature of PSA [9]. It can be concluded that the concrete workability is likely to be positively or negatively affected by the selected waterproofing admixture, depending on its type and dosage.

The effect of hydrophobic admixtures on the fluidity of self-compacting concrete (SCC) has been studied by a few researchers. Corinaldesi [59] used 45% emulsion of butyl-ethoxy-silane as a hydrophobic admixture, and a dosage of 1 kg/m³ was added to the SCC mixture. Rheological tests on cement pastes demonstrated that the addition of the hydrophobic admixture only slightly increased the

yield stress and plastic viscosity values, whilst the thixotropic behaviour was slightly reduced. Slump flow and V funnel tests conducted on the SCC showed that the hydrophobic admixture had a negligible influence on the slump flow but slightly increased the viscosity. Madduru et al. [60] used liquid paraffin wax as a hydrophobic admixture. When a dosage of 1% by weight of cement was added to SCC, its slump flow decreased from 780 mm to 735 mm, and the V-funnel flow time increased from 9.98 s to 10.55 s. Nonetheless, the influence of adding the hydrophobic admixture was not significant, and the fresh properties of the modified SCC still met the requirements of European guidelines for SCC. Tian and Qiu [61] studied the effect of a silane-based solution with a solid content of 40% on the flowability of self-compacting rubberised concrete. It is worth noting that the dosage of the hydrophobic admixture added to the SCC was relatively high (2–6% by the weight of cementitious materials or 11.7–35.2 kg/m³). It was found that increasing the hydrophobic admixture dosage slightly increased the viscosity and segregation resistance of the fresh concrete mixtures. However, in contrast with the findings reported by Madduru et al. [60], Tian and Qiu [61] found that the hydrophobic admixture slightly increased the flowability, filling ability, and passing ability of the SCC. For example, adding 4% hydrophobic admixture to the SCC without rubber increased its slump flow from 740 mm to 780 mm. Tian and Qiu [61] attributed this increase to the adsorption of hydroxyl groups from the hydrolysis of the silane/siloxane molecules on the surface of the cement particles, which reduced agglomeration and freed up the water that was previously confined by the agglomerated particles. In general, it seems that the influence of hydrophobic admixtures on the fluidity of SCC is not significant.

Only limited studies have been conducted on the effect of integral waterproofing admixtures on the setting time of concrete. Most waterproofing admixtures were found to shorten the setting time of concrete. It has been reported that calcium stearate reduced both the initial and final setting times of reinforced concrete, and the rate of acceleration decreased with increasing calcium stearate [47]. Spaeth [62] also reported shortened setting time of concrete treated with siloxane and silane. However, mortar samples containing two commercial waterproofing admixtures (Conplast X4211c and Conplast WP90) were reported to have prolonged initial and final setting times than the reference samples [63]. Meanwhile, the use of excessive amounts of hydrophobic admixtures may also result in prolonged setting time [64]. Therefore, trial tests would be advisable to check the setting time of concrete with an overdosed waterproofing admixture [65].

The impact of waterproofing admixtures on the concrete workability (i.e., slump) is important for choosing a suitable waterproofing admixture in field applications. For a specific application, a minimum slump value is often specified considering the distance between the reinforcement and ease of vibration, etc. When a waterproofing admixture significantly reduces the concrete workability, a higher amount of water or superplasticiser has to be added to achieve the target slump. Thus, it might adversely affect the concrete strength and shorten the durability and service life of the concrete. Therefore, caution must be exercised when using such waterproofing admixtures in real applications. It should also be noted that a waterproofing admixture might react with other concrete admixtures (e.g., superplasticiser) and jeopardise the properties of concrete. If there is no prior knowledge, trial tests are recommended to ensure that the designed concrete mix with a waterproofing admixture has suitable workability and setting time for field applications.

4.2. Effects of waterproofing admixtures on the mechanical properties

4.2.1. Compressive strength

Extensive research has been conducted to understand the influence of integral waterproofing admixtures on the strength properties of concrete. It would be favourable if an admixture has an insignificant or even positive influence on the concrete compressive strength. However, some waterproofing admixtures would cause a reduction in concrete compressive strength, which can be seen in the following discussion.

The use of siloxane- and silane-based materials as internal hydrophobic agents has been extensively studied, which demonstrated that the inclusion of those admixtures adversely affected the compressive strength of the treated concrete regardless of their hydrophobicity [23,54,66]. However, the reported reduction was normally within 20% when the admixture was added at a small dosage ($\leq 2\%$) [9,10,67]. The strength reduction could be attributed to the negative effect of silane on the hydration of C₃S in cement. In terms of the use of vegetable oils, researchers either reported an insignificant decrease or an improvement in compressive strength. The different results may be associated with the use of different dispersion agents [30,68,69], which could affect the air content in the hardened concrete [70].

In conventional concrete, the addition of a small amount of calcium stearate reduces the 28-day compressive strength up to 10%, and an optimum dosage (below 0.25% of cement weight) should be used without jeopardising the compressive strength of concrete [71]. It has also been reported that a high dosage of calcium stearate could improve compressive strength at a later age [10,47,72]. For example, the compressive strength of concrete in the presence of 3% calcium stearate increased from 22.3 to 37.1 MPa when the curing age increased from 28 to 60 days [47]. Also, the effect of calcium stearate on the compressive strength of lightweight foamed concrete (LFC) and self-consolidating concrete (SCC) has been studied. The results suggested that calcium stearate only retarded the strength development of LFC during the early ages (≤ 7 days) rather than reducing its compressive strength at 28 days or later [56]. The inclusion of a small amount of calcium stearate in SCC was found to have a minor influence on its compressive strength. When calcium stearate was used at a dosage of 1 kg/m³, the compressive strengths of 30 and 40 MPa SCC reduced by 6.1% and 0.5%, respectively; whereas that of 20 MPa SCC increased by 3.7% [73]. To compensate for any strength loss, a suitable amount of SCMs can be added to the concrete mixture together with calcium stearate. For instance, when 10% fly ash was added to 30 MPa SCC containing 1 kg/m³ calcium stearate, the 28-day compressive strength was increased from about 37 to 41 MPa [74]. On the other hand, it seems that a sufficient amount of calcium stearate should be used in concrete admixture to achieve a desirable reduction in water absorption. Research is still required to develop waterproof concrete by the combined use of calcium stearate and SCMs to avoid any loss in compressive strength at early ages.

Pre-treated hydrophobic admixtures usually have pozzolanic activity. By using up to 8% hydrophobic PSA, no significant adverse impact on the compressive strength of concrete was reported. At high replacement levels (12% and 50% PSA), a decrease in density and strength was witnessed due to increased air content in concrete [9]. The use of mechanically-modified hydrophobic slag was reported to reduce the early-age compressive strength by 15-30%, and an improvement in 28-day strength was found at a cement replacement level of up to 10% by weight [26]. Shi et al. [46] reported a slight improvement in the compressive strength of mortar treated with less than 10% chemically-modified hydrophobic slag due to the promotion of cement hydration. But when the hydrophobic slag was more than 10%, a larger required water-cement ratio and less cementitious material loosened the internal structure of the mortar, which decreased the bearing capacity.

An improvement in compressive strength was also reported by the addition of some complex water-repellent modifiers, such as siloxane-based polymer (SP) and potassium trimethylsilanolate (PT) [75,76]. These hydrophobisation modifiers contain sour tarring, sulphated melamine formaldehyde resins, soapstocks of vegetable oils, fly ash, triethanolamine, and fine rubber powder. A concrete strength increase of 15-20% was reported after adding the modifiers. It was reported that the 28-day compressive strengths of concrete increased from 39.6 to 45.8 and 42.1 MPa when Conplast X421Ic and Conplast WP 90 (two commercial water-repellent admixtures) were used, respectively [63]. It is worth noting that the ingredients of those commercial products are not known.

Some crystalline admixtures, such as sodium acetate, multi-crystallisation enhancers, silica-based crystalline admixtures, and LYN-1 (a commercial cementitious crystallising material), may improve the concrete compressive strength at 28 days [52,58,77]. For example, the compressive strength of concrete with 2% LYN-1 increased by 37% when the curing age increased from 7 to 28 days [52]. However, crystalline admixtures were reported to work better for concrete with a low w/c ratio (≤ 0.37). At a high w/c ratio (≥ 0.40), a strength loss of 20-30% (compared to the control concrete) has been reported by researchers when 2% and 4% silica-based crystallising admixture was used [63]. Al-Kheetan and Rahman [32] also reported a strength loss for concrete with a w/c ratio ≥ 0.40 after adding sodium acetate. A considerable reduction of 32% was reported for the 28-day compressive strength of a mix (w/c ratio of 0.46) containing 4% sodium acetate compared with the reference concrete. In contrast, some other researchers claimed that the addition of 3 to 4% sodium acetate into concrete with a w/c ratio of 0.54 had a negligible effect on the 28-day compressive strength [78]. The authors added 4% sodium acetate by the weight of cement in concrete with a w/c ratio of 0.53 and found a slight strength increase of 5% at 28 days [10]. It seems that the fineness of sodium acetate powder and the dispersion method might have an influence on the test results of cured samples. Due to the inconsistency of the results, further research is required to understand the effect of sodium acetate on the concrete compressive strength. Commercially available crystalline admixtures (e.g. Xypex C-1000) have also been used by researchers. García-Vera et al. [79] reported that the addition of Xypex C-1000 did not significantly affect the compressive strength of mortars in a non-aggressive environment. After 56 days of curing, the compressive strength of mortar with 1% Xypex C-1000 reduced by 3% in comparison with the strength of the control mortar, while mortar with 1.5 or 2% Xypex C-1000 experienced a strength increase by up to 28%. At 118 days, the difference in compressive strength between the Xypex-treated and untreated mortars was within 2-10%. It is worth noting that the treated mortar had a strength reduction of 7-20% when the curing age increased from 56 to 118 days. Another study found that the compressive strength of Xypex-treated concrete decreased significantly (between 35 and 45%) when the curing age increased from 7 to 28 days [80]. The compressive strength of normal concrete is expected to increase with increasing curing age. As ingredients in commercial products are not reported, it is hard to interpret their influence on concrete properties. There is no comprehensive research on the effects of different waterproofing admixtures on the compressive strength of concrete under different curing conditions (e.g., water, air, and dry curing).

The above discussion shows that hydrophobic admixtures often have a negative impact on the concrete compressive strength, causing a strength reduction of about 10% or more. This reduction is more noticeable at early ages (up to 28 days). The combined use of these admixtures with other materials, such as densifiers (e.g., SCMs), might be a good option to overcome the issue of strength reduction; however, this needs further comprehensive research. The effect of crystalline waterproofing admixtures on the concrete compressive strength is somewhat inconclusive, especially in the case of using commercial crystalline admixtures. As the compressive strength of concrete is often considered to be the most critical factor in determining the quality of concrete construction, trial tests on concrete mix with a new waterproofing admixture are recommended before its practical applications.

4.2.2. Flexural strength

Flexural strength, also known as modulus of rupture, reflects the concrete's ability to withstand bending. Whilst most integral waterproofing agents do not significantly affect the flexural strength of concrete, some admixtures were reported to have an obvious positive or negative influence [81]. Effects of curing age and dosages of waterproofing agents (naphthalene-based powder, polymer- and melamine-based liquids) on the flexural strength of concrete were studied by Geetha and Perumal [82]. At 7 days, the flexural strengths of concrete with polymer-, naphthalene-, and melamine-based admixtures were increased by 13-33%, 24-42%, and 20-40%, respectively, compared with that of the control concrete. However, at 28 days, the gains in flexural strengths dropped to 9-20%, 18-27%, and 11-30% for concrete with polymer-, naphthalene-, and melamine-based admixtures, respectively.

The use of vegetable oils was reported to reduce the flexural strength of concrete. At 28 days, the strength reduction was 15-23% [30,83]. The flexural strengths of SCC and LFC containing liquid paraffin wax and calcium stearate have been reported [56,60]. It is found that the paraffin wax increased the flexural strength due to retained moisture in promoting the C-S-H gel formation, whereas the effect of calcium stearate on the flexural strength was the opposite. As calcium stearate could delay the hydration of cement, the flexural strength development of concrete was delayed at early ages but would catch up at later ages. There is very limited research on the effect of commercial waterproofing admixtures on the flexural strength of concrete.

4.2.3. Tensile strength

Very limited research has been conducted to examine the effect of waterproofing admixtures on the tensile strength of concrete. The addition of calcium stearate was found to retard tensile strength development at early ages but had a minor influence at later ages [56]. This effect is similar to that of the flexural strength. The split tensile strength of SCC with liquid paraffin wax was reported to increase by 25-40% compared to that of the reference concrete [61]. In another study [84], the use of a hydrophobic admixture called Yellow River Engineering Consulting (YREC) improved the concrete's tensile strength by 30%. The YREC addition at an optimum percentage of 4% promoted the hydration reaction of cement and showed a filling effect on pores. Given the vast number of commercial and non-commercial waterproofing admixtures, more research is required to fully understand the effects of different admixtures on the tensile strength of concrete.

4.3. Effects of waterproofing admixtures on the dimensional stability

4.3.1. Drying and plastic shrinkages

Shrinkage is an inherent property of concrete, and excessive shrinkage could cause concrete cracking and reduce the durability of structures. Almost all existing studies [28,85,86] reported a decrease in drying shrinkage of concrete or mortar treated with various waterproofing admixtures, such as calcium stearate, perfluoroalkyl acrylate copolymer, and Adprufe™ 100. In contrast, Nunes and Slížková [87] found that silane emulsion had no obvious influence on the drying shrinkage of concrete. Gupta and Biparva [88] examined the influence of three commercially available crystalline waterproofing admixtures on restrained plastic shrinkage of concrete and found that the samples with waterproofing admixtures developed less plastic shrinkage than the reference concrete.

4.3.2. Creep

Creep directly affects the concrete's volume stability and leads to long-term deformation, internal stress redistribution, and prestress loss in prestressed concrete structures [89]. The creep behaviour of concrete with waterproofing admixtures has seldom been studied. Tkach et al. [75] presented experimental results of high-performance concretes with so-called hydrophobic tracers and complex hydrophobisation modifiers. An increase of 10-20% was found for the creep deformation of all treated concrete samples. The main reason for this is that the microparticles of surface-active substances were adsorbed on the surface of the growing crystals hydrosilicate, leading to a formation of a microcrystalline structure for the cement hydrates [75]. More research should be conducted to study the creep behaviour of concrete with other types of waterproofing admixtures.

4.4. Effects of waterproofing admixtures on the durability

The major purpose of using integral waterproofing admixtures is to increase the durability of concrete [1]. This section reviews the effects of integral waterproofing admixtures on various durability properties of mortar and concrete.

4.4.1. Sorptivity, water absorption and water permeability

The effects of different integral waterproofing admixtures on the water absorption, permeability and sorptivity of OPC concrete have been well studied. The addition of silane emulsion to mortar and concrete significantly decreases their capillary suction and water penetration [90], and the effect becomes more obvious with increasing amount of silane emulsion. Si-based powders were found to be effective in keeping the water repellency of concrete even after intense UV irradiation or abrasion of the concrete surface [91]. Zhu et al. [54] reported that silane-based hydrophobic admixture reduced the capillary water absorption of recycled aggregate concrete by 81% compared to the reference concrete. However, the compressive strength of the treated recycled aggregate concrete was significantly reduced.

Calcium stearate was found to reduce the water absorption rate and permeability of conventional concrete [74,76,92]. It is also effective in reducing the water absorption rate of SCC and LFC by up to 96% [56,73,93]. Its effectiveness can be further enhanced by more than 30% in the presence of fly ash in the mix [74]. Zheng et al. [94] and Ma and Chen [76] further evaluated the effects of various hydrophobic agents, including hydrophobic agent F, organic silicon hydrophobic agent, high fatty acids, siloxane-based polymer (SP), calcium stearate (CS), and potassium trimethylsilanolate (PT), on the water absorption of LFC. The water absorption reduced significantly as the content of SP, CS, or PT increased from 0.2% to 1.2%. It was found that SP was the most effective among the three hydrophobic agents. The 48-h water absorption of the LFC with 1.0% SP was reduced to 2.5% by volume, whereas the reference LFC had a corresponding water absorption rate of 3.6% [76]. High fatty acids were found to reduce the water absorption rate of LFC by 31.8% and were more effective than the hydrophobic agent F [94].

Yao et al. [95] investigated the effects of CS and sodium oleate (SO) on the water absorption of foamed concrete employing hydrogen peroxide as the foaming agent. The foamed concrete had densities in the range of 600-620 kg/m³. Because of its highly porous structure, the reference foamed concrete had a very high immersion water absorption of 35%. Although the foamed concrete with 1.2% CS or SO still had high water absorption (23-27%), the water absorption of the treated concrete was effectively reduced by 33% or 23% after adding the CS or SO in the mixture, respectively.

Water absorption of mortar and concrete treated with various vegetable oils from rapeseeds, soya beans, linseeds, peanuts, sunflower, olives, and corn, was found to decrease considerably [30,68,96]. Less water was absorbed by concrete when the amount of black olive oil [55] and linseed oil [96] was increased. However, Chandra and Xu [97] reported that concrete containing 0.5% corn oil did not reduce its capillary suction, which was in contradiction with the results reported by Justnes et al. [30]. This inconsistency may be due to the different methods used in dispersing the oil. Chandra and Xu [97] simply mixed the corn oil in the mixer with other ingredients, which might lead to an uneven distribution of the oil in the mixture.

Regarding the use of pre-treated hydrophobic admixtures, the addition of 15% hydrophobic GGBFS reduced the capillary water

absorption of lightweight mortar by up to 90% [26]. Because of the use of lightweight aggregates (0.09–4 mm), the density of the produced mortar was in the range of 1322–1430 kg/m³. Although the reported reduction in capillary water absorption in Ref. [26] was impressive, further research is required to study immersion water absorption of concrete with lightweight fine/coarse aggregate. Meanwhile, further research could investigate the effects of type, porosity, size and morphology of aggregates on the performance of waterproof concrete. Water absorption and sorptivity were reported to reduce by 83–84% and 83–86%, respectively, for concrete with 12% hydrophobic PSA compared to the reference concrete [9]. The effectiveness of hydrophobic PSA was proven for concrete even after vacuum saturation and immersion in water for 40 days. Thus, the concrete with hydrophobic PSA showed resistance to hydrostatic pressure to some degree [9]. It should be noted the PSA was used as cement replacement in Ref. [9] when the w/c ratio was kept constant. Hence, less water was used in concrete with PSA. Further research is required to investigate the effect of hydrophobic PSA on the water absorption of concrete with the same amount of water.

Sodium acetate and silica-based crystallising agents were found to be effective in decreasing the water absorption of concrete with low w/c ratios of 0.32–0.37 [57,77,98]. Nevertheless, the authors [10] found that sodium acetate was also effective in reducing the water absorption of concrete with a w/c ratio of 0.53 by about 50% after 60 days of curing. Some researchers have studied the effect of commercially available crystalline admixtures on the water absorption [79,80]. García-Vera et al. [79] concluded that Xypex only slightly decreased mortars' capillary water absorption. After the mortar samples were exposed to sulphuric acid for 90 days, no meaningful difference was observed between the treated and untreated mortars in terms of water absorption.

Different types of waste materials (such as waste glass, waste plastics, rubber tyres, and steel slag) can be used in concrete as aggregates or cement replacements. The impact of a particular waste material on the water absorption of concrete can vary depending on the type and quantity of the waste material utilised. For example, glass powder can be used to develop ultra-high performance concrete because its pozzolanic properties can be utilised to decrease the porosity of the concrete mix [99]. But the porosity and water absorption of concrete could increase with increasing content of glass aggregates. Abdulkadir and Mohammed [100] also reported inconsistent results regarding the effect of waste tires on the water absorption and permeability of rubberised concrete. While some researchers reported that the water absorption of concrete increased with an increase in rubber content, others reported the opposite [100]. Tian and Qiu [61] replaced 10–30% sand with crumb rubber by volume in making SCC. The 48-h capillary water absorption of the reference SCC was reduced from 0.83% to 0.60% when the rubber content increased from 0% to 30%. When 2% hydrophobic admixture was added, the capillary water absorption values of SCC with 0% and 30% rubber were reduced by 71% and 65%, respectively. The crumb rubber was less effective in reducing capillary water absorption of hydrophobic concrete than normal concrete. Furthermore, it was found that the crumb rubber had negligible influence on the 48-h immersion water absorption. It seems that caution must be exercised when using waterproofing admixtures in waste-based concrete.

This review shows that many hydrophobic and crystalline admixtures can reduce the water absorption rate of concrete by up to 80%. In practice, concrete can be exposed to either static or hydrostatic water pressure depending on the application scenario. For example, concrete pavements are often subjected to static water pressure only from rainwater. The use of hydrophobic admixtures for concrete pavements is suitable, considering that these admixtures often only reduce the water absorption under static water pressure. When concrete is exposed to hydrostatic water pressure (such as in water tanks and swimming pools), the combined use of hydrophobic admixtures with densifiers or crystalline admixtures may be more suitable. More research is required to completely understand the effects of different waterproofing admixtures and their combined uses on the water absorption and permeability of concrete under hydrostatic water pressure.

4.4.2. Chloride penetration

Steel reinforcement tends to corrode in chloride-contaminated concrete. Chloride penetration in integral waterproof concrete can be delayed, which might lead to a service life extension of reinforced concrete structures in an aggressive environment [66]. Chloride penetration tests are commonly performed to measure the electrical conductance of concrete and the depth to which chloride ions from the environment penetrate into the concrete. An addition of 2–4% silane emulsion by the weight of cement in concrete has been recommended to significantly enhance the chloride resistance of concrete [66,101]. When the reference concrete was exposed to a 3.1% NaCl solution for 72 h, chloride penetrated into the concrete up to a depth of approximately 12 mm. In contrast, the corresponding chloride penetration depth of the integral waterproof concrete with 4% silane emulsion was less than 6 mm, and the chloride concentration also decreased significantly (<0.6%) [102]. Similar beneficial effects were also reported for recycled aggregate concrete containing silane emulsion [54].

Incorporating calcium stearate in concrete also effectively decreased the chloride ion infiltration. In 20, 30, and 40 MPa concrete with 2–2.5% calcium stearate, the infiltration of chloride ions at a depth of 6 mm from the concrete surface decreased by 87, 69, and 113%, respectively, in comparison with the reference concrete [71]. The addition of calcium stearate of 1 kg/m³ in 20, 30 and 40 MPa SCC decreased the chloride ion infiltration by 8%, 32% and 15%, respectively, at 6 mm depth from the surface of SCC [73]. It is not clear why calcium stearate was less effective in SCC, and further study is required to clarify this. Although increasing the calcium stearate content might further reduce the chloride ion infiltration, a high content of calcium stearate will reduce the mechanical strength of concrete. A dosage of 1 kg/m³ was recommended for calcium stearate to be used in concrete mix design [29,71,73]. The addition of linseed oil in concrete also improved chloride resistance, especially at a dosage of 2% [96]. Similarly, the addition of 15% hydrophobic GGBS in lightweight concrete reduced the chloride penetration depth by about 90% at 63 days [26].

Crystalline admixtures are also effective against chloride ingress in concrete. Al-Kheetan et al. [57] prepared different concrete mixes with 2% or 4% of anhydrous sodium acetate. It was reported that the chloride diffusion was reduced by up to 90% in the depth range from 20 to 50 mm, especially for concrete with a low w/c ratio of 0.32 or 0.37.

The above-mentioned studies on the chloride resistance of waterproof concrete have shown promising results. The treated concrete

by either hydrophobic or crystalline admixtures showed a reduced chloride ion penetration and improved chloride resistance to a great extent. It may be inferred that there is a direct relationship between the water absorption rate and chloride resistance of concrete. However, further research is required to establish such a relationship for different admixtures.

4.4.3. Reinforcement corrosion

The corrosion of steel reinforcement in concrete structures is one of the most common reasons for infrastructure failure. Corrosion initiates due to the ingress of moisture, chloride ions, and carbon dioxide through the concrete to the steel surface [103]. After initiation, the volume of corrosion products (i.e. iron oxides) increases, leading to the formation of cracks and spalling of the concrete cover. This further exposes the reinforcement to a direct environmental attack and accelerates the deterioration of the structure. Therefore, a well-designed concrete mix can prolong the life of reinforced concrete structures [103].

Several studies have reported the effect of hydrophobic admixtures on the reinforcement corrosion in concrete. Most of these studies have focused on the effects of silane-based products. Tittarelli and Moriconi [104] found that the addition of silane emulsion inhibited the corrosion of reinforcing steel in uncracked concrete even with a very high w/c ratio of 0.80 when immersed in 3.5% chloride solution for one year. This was due to the effectiveness of the hydrophobic concrete in reducing water absorption and delaying chloride ingress. Simultaneously, they also tested cracked concrete specimens with a pre-determined crack width of 1 mm. In the presence of cracks, the hydrophobic concrete was less effective than the reference concrete in protecting the steel reinforcement from corrosion. Tittarelli and Moriconi [104] attributed this to the faster oxygen diffusion in the pores of the hydrophobic concrete, which were not saturated with water. The faster oxygen diffusion accelerated the steel corrosion. However, in another study conducted by the same authors [11], they found that the hydrophobic concrete containing silane emulsion could prevent the galvanised steel reinforcement from corrosion in both uncracked and cracked concrete with a w/c ratio of 0.45 or 0.75. Those specimens were exposed to wet-dry cycles in a 10% chloride solution. Tittarelli and Moriconi [11] claimed that the faster oxygen diffusion in the hydrophobic concrete promoted the passivation of galvanised steel reinforcement. To draw a firm conclusion on the effect of silane emulsion on steel corrosion, further research is required for both cracked and uncracked concrete. Tittarelli and Moriconi [105] reported that hydrophobic concrete with silane emulsion was more effective in protecting galvanised steel reinforcement from chloride-induced corrosion than the surface hydrophobic treatment.

Stearic acid emulsion [106] and calcium stearate [47] have been found to considerably improve the corrosion resistance of steel reinforcement. The corrosion resistance of reinforcement in SCC exposed to 3.5% NaCl solution for 60 days increased by 88.8% and 91.3% when the dosages of calcium stearate were 3 and 5%, respectively [47]. While stearic acid emulsion can only increase the hydrophobicity of concrete, calcium stearate also serves as an inhibitor of steel corrosion in concrete. Calcium stearate can be adsorbed onto the surface of steel through the polar carboxylate group forming insoluble hydrophobic salts on the steel surface [47]. However, these studies were only conducted on uncracked concrete specimens, and further research is required to check the effectiveness of stearic acid emulsion and calcium stearate in preventing steel corrosion in cracked concrete.

The above literature review indicates that contradictory results have been reported on reinforcement corrosion. For uncracked concrete, it seems that waterproofing admixtures are effective in protecting steel reinforcement from corrosion. But the efficacy of waterproofing admixtures is questionable for cracked concrete. Research should be conducted to further clarify this by testing various waterproofing admixtures, including crystalline admixtures (e.g., sodium acetate).

4.4.4. Carbonation

Compared with the durability properties of integral waterproof concrete reviewed in previous subsections 4.4.1–4.4.3, much less effort has been devoted to the study of other durability properties, such as carbonation, sulphate attack, acid attack, freeze-thaw resistance, alkali silica reaction, efflorescence, abrasion resistance, and long-term durability.

Concrete carbonation is due to the penetration of carbon dioxide (CO₂) into the porous concrete, leading to a decrease in pH. This might accelerate chloride-induced corrosion of steel reinforcement [107]. Only a few studies have examined the influence of waterproofing admixtures on the carbonation resistance of concrete and mortar. Zhu et al. [54] studied the carbonation rate of recycled aggregate concrete (RAC) treated with integral silane emulsion. The RAC had a w/c ratio of 0.5 and a compressive strength of 37 MPa at 28 days. Silane emulsion was added to RAC at a dosage of 0.5% or 1% by cement weight. The specimens were stored in a carbonation chamber with 4% CO₂. At 112 days, the carbonation depth of the RAC was about 20 mm, which was two times that of the counterpart with natural aggregate. This is because RAC is more permeable than normal concrete [108]. After adding 0.5% silane emulsion, the carbonation depth of the RAC was effectively reduced to 14 mm at 112 days. When the dosage of silane emulsion was increased to 1%, the carbonation depth dropped further to 12.5 mm. The slower carbonation rate of concrete with silane emulsion could be explained by its lower water absorption [108]. Vikan and Justnes [109] studied the influence of vegetable oils on mortar carbonation. The mortar had a w/c ratio of 0.5 and a cement-to-sand ratio of 1:3. The vegetable oil dosages were set to be 0.5%, 1.0% and 1.5% of cement weight. The carbonation of mortar samples in 5% CO₂ was monitored for 20 weeks. Surprisingly, it was reported that the addition of vegetable oils increased the carbonation depth of mortar samples. Vikan and Justnes [109] attributed this to the increased amount of macro pores in mortar samples with vegetable oils.

4.4.5. Sulphate attack

Sulphate attack is a complex damage phenomenon caused by the exposure of concrete to an excessive amount of sulphate from the external environment or internal sources (such as sulphate present in the aggregates or binder). Sulphate can react with calcium hydroxide (CH) and hydrated calcium silicate (C–S–H) in concrete to form expansive ettringite and gypsum, leading to concrete strength deterioration [110]. In the literature, only Wang et al. [111] reported the durability of waterproof mortar against sulphate attack, where commercially available polydimethylsiloxane (PDMS) was added to mortar at a dosage of 1% by cement weight. Mortar

samples were cured for 28 days and then soaked for one year in sodium sulphate aqueous solutions with mass percentage concentrations of 2%, 5%, and 10%, respectively. It was found that the addition of PDMS significantly reduced the mortar strength. While the reference untreated mortar had a 28-day compressive strength of 42.8 MPa, the corresponding strength of the PDMS-modified mortar dropped to 22.4 MPa. As expected, the strength of the reference mortar decreased significantly with increasing soak time in the sulphate solution, and the strength deterioration increased with increasing sulphate concentration. In contrast, the PDMS-modified mortar did not demonstrate strength deterioration. The improved resistance of the PDMS-modified mortar to sulphate attack was due to its reduced ingress of water and sodium sulphate [111].

4.4.6. Acid attack

The alkaline nature of concrete makes it vulnerable to acid attack, leading to the dissolution and leaching of acid-susceptible constituents in concrete (such as CH). Thus, the concrete has increased porosity, reduced cohesiveness, and decreased strength after the acid attack [112]. García-Vera et al. [79] studied the behaviour of mortars treated with a commercial crystalline admixture (Xypex Admix C-100 NF at a dosage of 1-2% of cement weight) in 3% sulphuric acid (H_2SO_4) solution. The samples were cured for 28 days before exposure to the acid attack. After 28 days of exposure to acid attack, the mix with 1.5% C-100 NF had the highest residual compressive strength of 48.9 MPa, which was higher than the corresponding strength (36 MPa) of the control mortar under acid attack and that (42.2 MPa) of the same mortar without exposure to acid. After 90 days of exposure to acid attack, all samples with or without C-100 NF exhibited a significant strength decrease. However, the samples doped with 1-2% C-100 NF had higher residual compressive strengths (21.8–24.1 MPa) than the control sample without crystalline admixture (18.8 MPa). The former had less mass loss after 40 days of exposure to acid attack than the latter.

García-Vera et al. [79] further studied mortar with zinc stearate (2% of cement weight) subjected to 3% H_2SO_4 attack. The samples were also cured for 28 days before exposure to an acid attack. The addition of zinc stearate slightly reduced the compressive strength. At 56 days, the compressive strengths of the unexposed samples with and without zinc stearate were 56 and 59.9 MPa, respectively. After the companion samples were exposed to the acid environment for 28 days, their corresponding strengths dropped to 44.4 and 53.7 MPa, respectively. In this scenario, the mix with zinc stearate had a strength reduction of 20.7% due to the acid attack, which was even greater than the corresponding reduction of 10.4% for the control mix. After 90 days of exposure to acid attack, the corresponding strengths of the samples with or without zinc stearate further dropped to 40.6 and 41.7 MPa, respectively. At this moment, the residual strengths of the two mixes were very close, and the use of zinc stearate did not have a positive effect on maintaining the compressive strength. Despite this, the open porosity of the samples with zinc stearate was still much lower than that of the reference samples. By comparing the results of zinc stearate-doped and C-100 NF-doped mortars, it may be concluded that the crystalline admixture C-100 NF performed better in improving the acid resistance of mortar than zinc stearate. It seems that the former could directly block pores in concrete, which requires more research to provide further insights.

Microbial-induced corrosion is an unresolved issue for concrete sewer systems, which is mainly caused by the attack of H_2SO_4 generated by the microbial ecosystem in sanitary sewer conduits [112]. Soroushian et al. [112] conducted field and laboratory tests to examine the efficacy of commercial water-repelling additives in reducing the microbial-induced corrosion of concrete sewer systems. RHEOPEI manufactured by BASF was added to the concrete at a dosage of 19.8% or 38% of the total weight of cement and silica fume. In the lab tests, the concrete specimens were cured for 28 days and then immersed in 3% H_2SO_4 solution for 90 days. The test results demonstrated that the hydrophobic concrete had a lower loss of thickness and higher flexural strength than the reference concrete after the acid attack, showing the benefits of using hydrophobic concrete. Then Soroushian et al. [112] conducted field tests by exposing the samples to an aggressive sanitary sewer environment for up to 11 months. Surprisingly, the hydrophobic concrete demonstrated more severe damage than the reference concrete in the field, which was contradictory to the observation in the laboratory. Although the reason behind this is not known, it can be concluded that the lab condition could not fully represent the real sewer environment. Further research is required in this area.

4.4.7. Freeze-thaw resistance

Freezing-thawing is the leading cause of the degradation of concrete structures and pavements in cold regions [113]. During the cyclic freeze-thaw process, the internal pores of the concrete are damaged, causing scaling of the concrete surface, mass loss, increased water absorption, and strength deterioration. Theoretically, the addition of waterproofing admixtures can improve the freeze-thaw resistance of concrete, as less water is transported into the cement matrix of concrete [9]. However, a waterproofing admixture might negatively affect the concrete strength, which could lead to reduced freeze-thaw resistance.

Only a few researchers studied the freeze-thaw resistance of integral waterproof concrete. Ma et al. [113] added silane emulsion to a concrete mixture at a dosage of 2% or 4% of cement weight. The concrete samples were cured for more than one month before subjecting to freeze-thaw cycles ($-17^\circ C$ to $+8^\circ C$). The use of silane emulsion significantly reduced the concrete strength. A strength reduction of 17.9% was reported when 4% silane emulsion was added to the concrete with a w/c ratio of 0.4. After experiencing 50 freeze-thaw cycles, the compressive strength of the reference concrete without silane emulsion reduced from 57.6 MPa to 39.2 MPa, whereas the compressive strength of the concrete with 4% silane emulsion reduced from 47.3 MPa to 21.9 MPa. As can be seen, the strength loss of the concrete with silane emulsion was 53.7%, which was even more than the strength loss of 31.9% for the reference concrete. Meanwhile, it was found that the freeze-thaw resistance of concrete reduced with increasing dosage of silane emulsion. Ma et al. [113] concluded that the silane emulsion retards the hydration of cement, which might disrupt the microstructure of concrete and reduce its freeze-thaw resistance. Similar findings were also reported by Rogers et al. [114] and Weise et al. [115], who used either silane-based commercial products or vegetable oils as hydrophobic agents.

Zhang et al. [116] developed a hydrophobic agent named Yellow River Engineering Consulting (YREC), where mica powder was

used as the substrate pretreated with a silane coupling agent. The pretreated powder was then coated with a polydimethylsiloxane modifier. YREC was added to concrete at a dosage of 2–4% by weight of cement. Unlike silane emulsion, YREC was found to accelerate cement hydration. For this reason, adding YREC could increase concrete strength, especially at early ages. After curing for 28 days, concrete samples were exposed to freeze-thaw cycles ($-18\text{ }^{\circ}\text{C}$ to $+10\text{ }^{\circ}\text{C}$). The concrete failure was defined as the moment when the loss in dynamic elastic modulus reached 60%. It was found that the reference concrete with a w/c ratio of 0.5 failed after 35 freeze-thaw cycles. However, concretes with 2%, 3% and 4% YREC failed after 83, 89, and 111 freeze-thaw cycles, respectively. It appears that the addition of YREC improved the freeze-thaw resistance of concrete. Zhang et al. [116] attributed this to the improved pore network after adding the admixture, which reduced the water absorption by up to 18.5%.

More recently, Al-Kheetan et al. [57] studied the freeze-thaw performance of concrete with sodium acetate. Four concrete mixtures were developed with w/c ratios of 0.32, 0.37, 0.40, and 0.46, respectively. Sodium acetate was added at two different ratios: 2% and 4% of cement weight. The freeze-thaw test was run for 6 months with temperatures changing from $-10\text{ }^{\circ}\text{C}$ to $+6\text{ }^{\circ}\text{C}$. For concrete with a low w/c ratio (0.32 or 0.37), the addition of sodium acetate improved its freeze-thaw performance, which was observed based on the reduced concrete scaling and mass loss after testing. However, the inclusion of sodium acetate in concrete with a high w/c ratio (0.40 or 0.46) reduced its freeze-thaw resistance. After adding 4% sodium acetate, the mass loss of the concrete with a w/c ratio of 0.37 was about 4% when tested in water. But the corresponding mass loss of the concrete with a w/c ratio of 0.46 increased to 7.7%, which was even higher than the untreated concrete. Al-Kheetan et al. [57] explained that sodium acetate reduced the capillary water in the concrete with a low w/c ratio, which improved its freeze-thaw resistance as capillary water is subjected to frost action. However, sodium acetate increased microcracks and the content of air voids in concrete with a high w/c ratio, which reduced its freeze-thaw resistance.

Research on freeze-thaw resistance of concrete with either hydrophobic or crystalline admixtures has shown both positive and negative impacts. Further comprehensive research is required to investigate the effect of combined use of different waterproofing admixtures on the freeze-thaw durability of concrete. In practice, air-entraining admixtures are often used to improve the resistance of concrete against freezing and thawing. The combined use of waterproofing and air-entraining admixtures should also be studied for practical applications.

4.4.8. Alkali silica reaction

The alkali-silica reaction (ASR) is a slow reaction between the highly alkaline cement paste and reactive silica in aggregates, forming a hygroscopic sodium silicate gel. The gel can swell by absorbing water, causing cracking and spalling of concrete [117]. It is postulated that ASR might be mitigated if the available moisture within concrete could be reduced. This has motivated researchers to use silane surface treatment to mitigate ASR. However, contradictory results have been reported in the literature [118,119]. Although silane itself is hydrophobic, water vapour can still transport into the treated concrete for a prolonged period.

The use of integral waterproofing admixtures has seldom been tried to mitigate ASR. Weise et al. [115] added a silane/siloxane-based hydrophobic agent to concrete at a dose of 2% by cement weight. This led to a significant reduction of 24% in compressive strength at 28 days. However, it was found that the hydrophobic concrete also had a significant reduction in moisture and deicing salt penetration. Thus, the ASR damage of the hydrophobic concrete was greatly reduced compared with the reference concrete. Based on the test results, Weise et al. [115] claimed that hydrophobic agents could potentially enable the use of borderline alkali-sensitive aggregates in concrete pavements. Considering the very limited research on this topic, more tests are required to study the effectiveness of different waterproofing admixtures in mitigating ASR under different conditions (such as cracked concrete under drying/wetting cycles).

4.4.9. Efflorescence

Efflorescence is the deposit of white salts (e.g., CaCO_3 , Na_2CO_3) slowly migrating towards the concrete surface with the aid of moisture or water [120]. For OPC concrete, efflorescence is normally considered harmless except for a decline in aesthetic appearance. But for geopolymer concrete (GPC) made with source material rich in silica and aluminium, efflorescence could be a major issue due to the use of a large amount of water-soluble alkali activators. This is particularly a concern for conventional GPC activated by sodium hydroxide and sodium silicate solutions. Efflorescence not only leads to inferior aesthetic appearance but also structural damage to GPC [121].

Pasupathy et al. [122] used commercially-available hydrophobic fumed silica and silane crème (a mixture of silane and siloxane) to control the efflorescence of GPC. They made hydrophobic sand first by coating the sand with 1–2% fumed silica or 10–20% silane crème by weight of the precursor (i.e., fly ash and slag). The treated sand was then added to the GPC mixture. After curing, the GPC specimens were kept in contact with water at the bottom surface for 7 days to observe the formation of any efflorescence. It was reported that the use of silane crème reduced the compressive strength of GPC by up to 33% due to the hindrance of the geopolymerisation reaction. In contrast, the use of hydrophobic fumed silica enhanced the compressive strength of GPC by up to 20% due to the filler effect. Meanwhile, all samples with hydrophobic sand had reduced surface-salt accumulation because of reduced capillary water absorption and increased surface hydrophobicity of the GPC. In general, hydrophobic fumed silica was more effective than silane crème in controlling the efflorescence of GPC, because the former could not only form hydrophobicity but also densify the microstructure of GPC. The addition of 2% fumed silica completely eliminated the formation of efflorescence in GPC.

Chindaprasirt et al. [120] made a lightweight fly ash-based geopolymer cured at $65\text{ }^{\circ}\text{C}$ for 24 h. Fly ash was replaced by 1–10 wt% calcium stearate to increase hydrophobicity. The inclusion of calcium stearate in geopolymer slightly reduced its density (up to 14.8%) but significantly reduced its strength. The reference geopolymer and the one with 10% calcium stearate had compressive strengths of 5.4 MPa and 1.8 MPa, respectively. Meanwhile, the inclusion of calcium stearate also increased the water absorption of the geopolymer

immersed in water for 24 h. This is due to the increased pores in geopolymer with the addition of calcium stearate. However, by incorporating 5% or 10% calcium stearate into the mixture, the issue of efflorescence was effectively eliminated.

4.4.10. Abrasion resistance

The influence of waterproofing admixtures on the abrasion resistance of concrete or mortar has not been the focus of previous studies. The result of abrasion tests on hardened cement mortar treated with PDMS showed that the treated mortar surface was mechanically strong against repeated abrasion, associated with its integral water repellency [123]. Al-Rashed and Jabari [58] reported the results of the abrasion resistance of concrete treated with a multi-crystallisation enhancer (MCE). Increasing the MCE dosage increased the abrasion resistance significantly due to the improvement of concrete strength. This enhancement in the abrasion resistance of concrete with MCE agrees with a previous study on a similar crystallisation system using surface treatment for hardened concrete [58]. It is worth noting that some waterproofing admixtures can reduce concrete strength, as mentioned earlier. In this case, the abrasion resistance of concrete might be reduced. Further research is required in this area.

4.4.11. Long-term performance

The long-term performance of integral waterproof concrete is a topic of great interest to many engineers and researchers, but such tests are normally very time-consuming. Cusson et al. [124] used a hydrophobic admixture in concrete slabs of a parking building, which had experienced concrete cracking and reinforcement corrosion. The damaged slabs were demolished and replaced with new slabs. To compare with normal concrete, hydrophobic concrete was used in two sections of a slab, where a commercial hydrophobic admixture was added at a dose of 30 L/m³ as a pore blocking ingredient. A membrane was applied to the surface of normal concrete to prevent moisture from entering the inner part, but no membrane was installed on the hydrophobic concrete section to check its effectiveness in blocking moisture penetration. The concrete slabs were monitored for two years after reconstruction. No obvious difference was found between the hydrophobic concrete and reference concrete in terms of drying and thermal expansion. Deep cracks occurred in both types of concrete, and the hydrophobic concrete was found ineffective in preventing the migration of moisture through the floor.

Robertson and Newton [125] reported test results of 25 reinforced concrete panels exposed to a marine tidal environment for five years. Commercial admixtures, including Xypex Admix C-2000 and Kryton KIM, were used to reduce concrete permeability and prevent or delay reinforcement corrosion. Half-cell potential tests were performed to evaluate the corrosion possibility. The higher the half-cell readings, the higher the possibility of reinforcement corrosion. Compared with the control panels and the ones with Xypex Admix C-2000, the panels with Kryton KIM had significantly improved corrosion resistance.

Dao et al. [126] also studied the feasibility of using permeability-reducing admixtures to prevent chloride-induced corrosion of steel reinforcement in marine concrete structures. Two commercial admixtures were used: one was crystalline admixture (C), and the other was hydrophobic with pore-blocking effects (HPI). C admixture was added at a dosage of 4 kg/m³, and HPI admixture was added at a dosage of 30 kg/m³. Short reinforced concrete columns (350 mm in width and 750 mm in height) were cast and exposed to a simulated coastal environment in the lab for two years. While C admixture had negligible influence on the concrete strength, HPI admixture reduced the 28-day compressive strength by 10%. It was also found that the HPI admixture considerably enhanced the resistance to chloride-induced corrosion, but the inclusion of C admixture had no detectable effect on the onset of corrosion.

Spaeth et al. [91] investigated the influence of accelerated ageing, including rain/sun cycles and UV radiation, on the hydrophobic performance of mortar samples incorporated with siloxane and silane-based hydrophobic admixtures. Some mortar specimens were exposed to UV light for 672 h, whereas the others were aged in a climatic chamber for 28 days and subjected to a total of 112 sun/rain cycles. The ageing tests generally proved the excellent long-term hydrophobicity of the samples subjected to rain-sun cycles or UV radiation, indicating the benefits of the integral hydrophobic modification. However, this was only true for siloxane and silane-based admixtures that could form cross-linked network in the cement matrix. When silanol-terminated polydimethyl siloxanes were used, they could leach out during the ageing test because of their low reactivity with the cement matrix. Accordingly, the hydrophobicity of the corresponding mortar samples was reported to deteriorate with an increasing ageing period.

5. Challenges and future research perspectives

As reviewed in Section 3, there are many different types of waterproofing admixtures, which can be used solely or in combination with each other. Accordingly, many commercial products were developed with the aim to reduce the water absorption of concrete and increase its durability. However, a study conducted by the Concrete Society in the UK [5] cast serious doubts on the benefits claimed by some manufacturers. In fact, many commercial admixtures contain a high amount of superplasticiser and SCMs, which effectively decrease the water/binder ratio and result in denser concrete. Hence, caution must be exercised while evaluating the waterproofing capacity of such products. The authors [10] recently also evaluated the effectiveness of six commercial integral waterproofing admixtures on the water absorption, slump, and compressive strength of concrete with a w/c ratio of 0.53 and a target 28-day compressive strength of 40 MPa. The admixtures were added to the concrete strictly following the manufacturers' instructions. The test results showed that one of the commercial admixtures even slightly increased the water absorption rate of concrete. The rest five commercial admixtures indeed decreased the water absorption rate, but none of them could meet the water absorption limits specified in Refs. [6,7] for waterproof concrete. In the tests, the most effective commercial admixture only decreased the concrete water absorption by 21%. Inconsistent results of commercial admixtures were also reported by other researchers [112,124–126], which have been reported in earlier sections. More research is required to develop economical and effective waterproofing admixtures, which will increase the confidence of the construction industry in waterproofing admixtures.

Most integral waterproofing admixtures consist of a single functional waterproofing agent and additional mineral compounds [58,

127]. However, a single waterproofing admixture would be very challenging to meet the many design requirements for concrete durability, such as chloride penetration, reinforcement corrosion, and carbonation. It is an interesting idea to combine admixtures with different mechanisms of waterproofing, but very little research has been conducted in this direction. Al-Rashed and Al-Jabari [58] developed a multi-crystallisation admixture, which combines hygroscopic and hydrophilic crystals with a hydrophobic characteristic. Some manufacturers also claim that their products have both hydrophobic and crystalline compounds [126]. However, vigorous research is required to check the effects of such complex admixtures on the fresh, mechanical, and durability properties of concrete.

Currently, there is a lack of guidelines to determine the efficacy of waterproofing admixtures, and the sample preparation processes are also not consistent. Researchers tend to make concrete with a specific w/c ratio and then vary the dosage of a waterproofing admixture. But different practices have been adopted in demoulding (with or without demoulding agents), curing (controlled or uncontrolled conditions), and drying (temperature and duration) their concrete samples [128]. The efficacy of the waterproofing admixture is often judged by the reduction in water absorption, which is relatively easy to measure. Since the concrete mix designs and test procedures are often different, it is not straightforward to compare the test results in different studies. While water absorption is an important parameter, the effects of waterproofing admixtures on some important durability properties (e.g., reinforcement corrosion, carbonation, acid resistance) should also be tested to judge the efficacy of the admixtures.

Most of the previous studies have focused on the compressive strength and water absorption of integral waterproof concrete, and limited efforts have been devoted to investigating its durability properties. Meanwhile, the toxicity and environmental impact of waterproofing admixtures should also be studied. In particular, there is a lack of long-term field monitoring of integral waterproof concrete. When using waterproofing admixtures, a premium needs to be paid, which increases the construction cost. Due to inadequate research on the durability of integral waterproof concrete, it is not possible to accurately predict the increase in the service life of concrete structures and infrastructure for the use of waterproofing admixtures. Further research is required to assess the long-term benefits of using integral waterproof concrete based on life cycle assessment.

Previous studies have mainly focused on OPC concrete. In recent years, alkali-activated concrete (e.g., GPC) has been attracting increasing research interest as a promising alternative to OPC concrete to reduce carbon emissions from construction activities [129]. A few studies [130] have been conducted to treat GPC with a surface coating to reduce its water absorption. However, very little attention has been paid to developing waterproof alkali-activated concrete [122]. It should be noted that waterproofing admixtures developed for conventional OPC concrete might not work in alkali-activated concrete. For instance, sodium acetate has been recognised as an effective waterproofing admixture for OPC concrete [10]. However, it cannot be used in GPC due to the chemical reaction between the sodium acetate and sodium hydroxide in the mixture; the reaction produces methane and generates pores inside the concrete. Further work is required to develop waterproof alkali-activated concrete with high performance and cost effectiveness.

6. Conclusions

This paper has conducted a comprehensive review of integral waterproof concrete. Mechanisms and limitations of different types of waterproofing admixtures were reviewed first. Then the effects of waterproofing admixtures on the concrete's fresh, mechanical and durability properties were summarised. Finally, challenges and future perspectives in developing integral waterproof concrete were presented. The following conclusions can be drawn from this study:

- (1) Waterproofing admixtures can be roughly classified into three groups: densifiers, water repellents, and crystalline admixtures. Because of the limited efficacy, densifiers cannot be used alone to develop waterproof concrete. Water repellents are suitable for non-critical areas with low water tables or above-ground applications. Crystalline admixtures can form crystals in concrete with pore-blocking effects and are suitable for structures under hydrostatic conditions. Currently, there is a trend to develop admixtures with hydrophobic and crystalline compounds. But rigorous research is required to check their effects on different concrete properties.
- (2) Water repellents tend to reduce concrete strength, which is especially true for silane/siloxane-based products. To compensate for the strength loss, a suitable amount of densifiers, such as supplementary cementitious materials, can be added to the concrete mixture. The effect of crystalline admixtures on the concrete compressive strength is somewhat inconclusive, especially in the case of using commercial crystalline admixtures.
- (3) Waterproofing admixtures have a tendency to reduce drying shrinkage and plastic shrinkage of concrete.
- (4) Researchers have consistently reported the reduction of concrete water absorption by up to 80% after using waterproofing admixtures. They also reported reduced chloride penetration in integral waterproof concrete. However, contradictory results have been reported on reinforcement corrosion. For uncracked concrete, waterproofing admixtures are effective in protecting steel reinforcement from corrosion. But the efficacy of waterproofing admixtures is questionable for cracked concrete.
- (5) Integral waterproof concrete might have increased resistance to carbonation, provided that the waterproofing admixture does not negatively affect the microstructure.
- (6) The addition of waterproofing admixtures can improve the freeze-thaw resistance of concrete, provided that the concrete strength is not significantly reduced. Furthermore, waterproofing admixtures also have the potential to mitigate alkali-silica reaction and efflorescence of concrete.

It is worth noting that reports on the efficacy of commercial waterproofing admixtures are inconsistent. More research is required to develop economical and effective waterproofing admixtures, which will increase the confidence of the construction industry in waterproofing admixtures. Meanwhile, there is a need to develop proper guidelines on sample preparation and determination of the efficacy of waterproofing admixtures. The toxicity and environmental impact of waterproofing admixtures should also be studied.

Further work is required to develop waterproof alkali-activated concrete with high performance and cost-effectiveness. Moreover, the effect of waterproofing admixtures on the concrete creep has seldom been studied. Only one study reported an increase of 10-20% in creep for their hydrophobic concrete. Very limited studies have been conducted on integral waterproof concrete subjected to sulphate or acid attack. It appears that the integral waterproof concrete has improved resistance to chemical attacks. However, it is inconclusive in terms of the microbial-induced corrosion of integral waterproof concrete when used in concrete sewer systems. Further research is required in this area. Finally, very limited research has been conducted on the long-term performance of integral waterproof concrete in both laboratory and field, and the reported conclusions are contradictory. Therefore, further research is required to assess the long-term benefits of using integral waterproof concrete based on life cycle assessment.

Declaration of competing interest

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Data availability

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